SCIENCE FOR GLASS PRODUCTION

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SOLUBILITY OF COPPER-CONTAINING CALCIUM – PHOSPHATE GLASSES

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The solubility of copper-containing calcium – phosphate glasses is determined as a function of the ratio $CaO : P_2O_5$, Al_2O_3 additions, and CuO content. The glasses are characterized by high solubility in boiling water. The recorded flow of copper ions into the water ranges from 60 to 125 ppm; this makes it possible to classify the synthesized glasses as biocides. The ratio of the modifying cations and glass former, determining the structure of the phosphorus – oxygen framework of the glass, has the greatest effect on the solubility of the glass; the introduction of Al_2O_3 and substitution of copper oxide for calcium oxide has the weakest effect.

Key words: calcium – phosphate glass, biocide component, copper ion, solubility, mass losses, ion yield.

Phosphate glasses are promising materials with many uses. At present they are used in optics, laser technology, as glassy protective coatings on aluminum, and elsewhere. In recent years these glasses and glass ceramics based on them have started to be used in medicine as biologically active materials with the capability of controlled dissolution (degradation) in physiological media accompanied by the release of ions of phosphorus, calcium, and other elements required for regeneration of bone tissue [1]. The capability of phosphate glasses doped with different ions to undergo prolonged dissolution opens up new possibilities for using them as inorganic ion carriers; for example, in medicine for localized delivery of ions to a sick organ (RF Patent No. 97103529), in the general economy as mineral fertilizer with prolonged action (RF Patents Nos. 2079475 and 2130006), in the chemical industry as catalyst carriers, and elsewhere.

It is of practical interest to use bivalent copper Cu^{2+} as the ion introduced: it exhibits strong bacteriocidal action and is much less expensive than silver [2, 3]. These glasses could become the basis for the development of glassy disinfecting filtering materials, bacteriocidal fibers, and glass fabric [4], antibacterial coatings with prolonged action, and so on. To design such materials it is necessary to know the level, kinetics, and mechanism of the dissolution of phosphate glasses with different chemical composition.

It is known that the interaction of phosphate glasses with water media differs fundamentally from that for silicate glasses. The main difference is that high-silica hydrolyzed layers, possessing protective properties and slowing the interaction right down to stopping it completely, form on the surface of silicate glasses as a result of leaching and hydrolysis. Such layers do not form on the surface of phosphate glasses, the interaction process continues and if special measures are not taken, it can lead to complete degradation of the material. Alkali-containing phosphate glasses are distinguished by especially high solubility. A study of the dissolution of sodium-calcium-phosphate glasses with small additions of silica [5] showed that the glass-mass losses and the concentration of the products of interaction in the solution depend linearly on treatment time and do not stabilize on contact with the medium for up to 4000 min, i.e., the rate of dissolution of the glass remains constant in time.

In the present work we study the solubility of copper-containing calcium-phosphate copper-containing glasses in water as a function of the basic composition of the glass and its copper content.

Glass with variable ratio $CaO : P_2O_5$ and constant B_2O_3 and CuO content (series I), glass with Al_2O_3 additions (series II), and glass with variable composition CaO : CuO and constant P_2O_5 and B_2O_3 content (series III) were synthesized for these investigations (Table 1).

The initial materials used were reagent-pure and analytically-pure: calcium carbonate, copper oxide, aluminum oxide, boric acid, and orthophosphoric acid (85% solution). Synthesis was conducted in a laboratory electric furnace at temperatures 1250 – 1300°C with soaking time 15 min, after which product was removed onto a glass plate. The glasses

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were ground in a porcelain mortar and the 0.5 – 0.8 mm fraction was extracted. The samples were stored in a drier to prevent interaction with the moisture in air.

The solubility of the glasses was determined according to the mass loss, the migration of copper, calcium, and phosphorus ions into the solution, and the pH of the medium after a weighed amount of glass powder with mass about 1 g was boiled in distilled water (100 ml) for 1 h. The mass losses were determined by weighing the samples before and after boiling; the migration of calcium ions was determined by measuring the potential of the calcium electrode in the standard and experimental solution on an I-160M laboratory ion meter; the migration of phosphate ions and copper ions was measured by the method of differential photometry on a KFK 2MP photoelectrocalorimeter; the pH of the solutions was measured with an I-160M laboratory ion meter.

All synthesized glasses with the exception of compositions with $CaO : P_2O_5 = 1.25$ (total content of the modifying ions $CaO + CuO = 60\%$[3]) were satisfactorily made and fined. The glass color varied from light blue to dark green depending on the CuO content. The glasses with $CaO : P_2O_5 = 1.25$ crystallized intensely during production.

The solubility levels of the synthesized glasses (boiling in water for 1 h) are presented in Table 2. The glasses obtained are characterized by high solubility in water: mass losses reach 5%, ion outflow is unstable, and the water medium becomes acidic after interacting with the glass.

As the total amount of the modified oxides in series I and II glasses increases, the mass loss changes by a factor of 4 – 5, and other indicators also change significantly. The highest solubility is reached in compositions of this series with maximum content of the glass former P_2O_5 ($CaO : P_2O_5 = 0.5$).

The change of the solubility of the series I and II glasses (without and with Al_2O_3) as a function of the main composition is similar — as the content of the modifying components increases to $CaO : P_2O_5$ ratio about 1 (which corresponds to the total content $CaO + CuO \approx 50\%$), the solubility sharply decreases and them somewhat stabilizes or increases (Figs. 1 and 2). Evidently, such concentration dependences of the solubility are due to a change of the structure of the phosphorus – oxygen framework of the glasses.

It is known [6 – 9] that the three-dimensional ultraphosphate structure of glasses which is characterized by modifier-ion content less than 50% possesses low water resistance because of the presence of a large number of hydrolytically unstable branching points — $[PO_4]^{3-}$ structural elements with three bridging oxygen atoms (Fig. 3). Because of the excess negative charge, localized on nonbridging oxygen, bound with phosphorus by a double bond, the energy balance of the entire structural element is disrupted, which results in easy hydrolyzation of the P – O bonds. In the experimental glasses, the calcium and copper ions play the role of modified ions; the total content of their oxides is less than 50% in compositions with $CaO : P_2O_5 = 0.5$. These compositions are characterized by an ultraphosphate structure and manifest the highest solubility with respect to all indicators studied.

As the total content of the modified cations increases to about 50%, the ultraphosphate structure of the glasses transforms into a metaphosphate structure characterized by long

TABLE 1.

Series I, molar content		Series II, molar content			Series III, molar content, %	
$CaO : P_2O_5$	CaO + CuO, %	$CaO : P_2O_5$	Al_2O_3, %	CaO + CuO, %	CaO	CuO
0.50	42	0.50	4	42	32	0
0.70	48	0.70	4	48	24	8
0.90	53	0.90	4	53	16	16
1.10	57	1.10	4	57	8	24
1.25	60	1.25	4	60	0	32

TABLE 2.

Indicator	Series I	Series II	Series III
Mass losses, %	1.0 – 4.6	0.5 – 2.0	3.2 – 5.5
pH	3.5 – 6.6	4.3 – 6.5	3 – 5
Ion outflow, ppm:			
calcium	4 – 320	3 – 220	0 – 600
copper	81 – 92	60 – 83	65 – 125
Phosphate ion outflow, mg/liter	190 – 340	70 – 210	70 – 210

[3] Here and below — molar content.

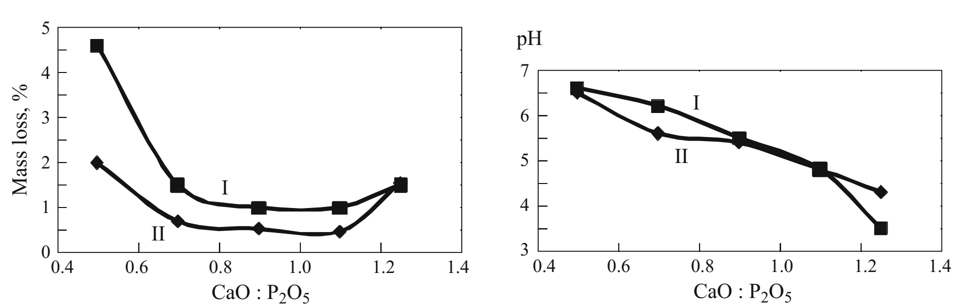

Fig. 1. Mass loss and pH of the solutions obtained after boiling of series I and II glasses.

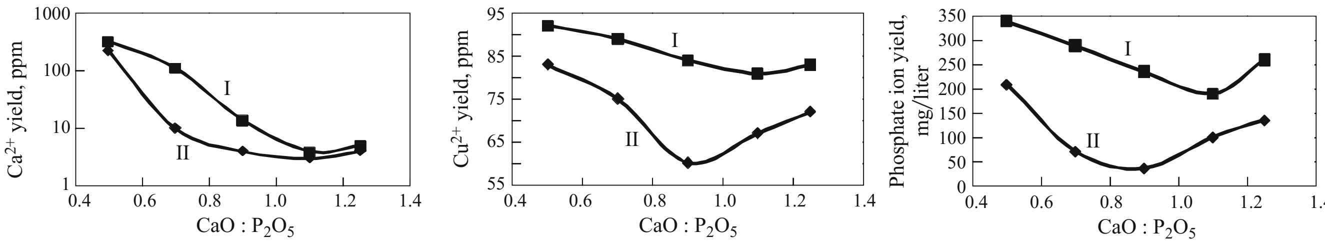

Fig. 2. Migration of calcium, copper, and phosphate ions into solution after boiling of series I and II glasses.

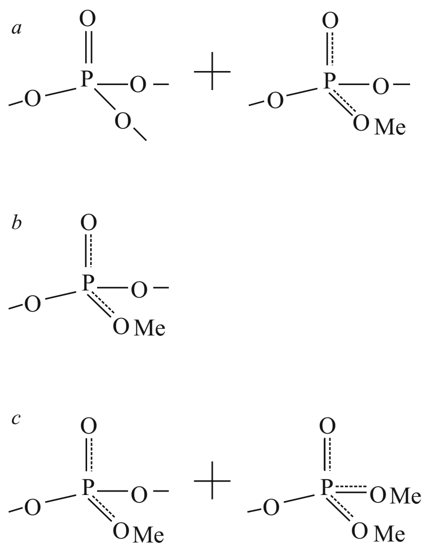

Fig. 3. Structural elements of phosphate glasses with different content of the modified cation (Me): *a*) elements of the ultraphosphate structure, MeO : $P_2O_5 < 1$; *b*) elements of the metaphosphate structure, MeO : $P_2O_5 = 1$; *c*) elements of a polyphosphate structure, MeO : $P_2O_5 > 1$.

phosphorus-oxygen chains whose $[PO_4]^{3-}$ structural elements contain, as a rule, two bridging oxygens. There are few branching points in such a structure because of the redistribution of the electron density and some neutralization of the excess negative charge. The conversion to the metaphosphate structure is accompanied by a sharp decrease of the solubility, manifested in the dependences obtained when CaO : P_2O_5 = 0.7 – 0.9.

A polyphosphate structure forms with higher modifier content in the glasses (CaO : P_2O_5 > 0.9 with CaO + CuO > 50%). This structure is characterized by shorter phosphate chains and the formation of terminal phosphate groups, which have three nonbridging oxygen ions. According to the results of modern studies, the bivalent modifier ions present in the polyphosphate glasses "sew together" the terminal phosphate groups, strengthening the phosphorus – oxygen framework and stabilizing the degree of hydrolytic stability attained. Some data show that the chemical stability of polyphosphate glasses, for example, glasses in the system $(50 - x/2)Na_2O - xCuO - (50 - x/2)P_2O_5$ with $x = 33.3\%$, increases appreciably [10].

In the glasses studied in the present work, stabilization of the solubility indicators at a definite level is observed on the whole for CaO : P_2O_5 = 0.9 – 1.1 (CaO + CuO = 50 – 57%). However, for CaO : P_2O_5 = 1.5 (CaO + CuO = 60%) an increase of solubility is observed in series I and II glasses; all indicators studied point to this (see Figs. 1 and 2). Apparently, this is explained by the crystallization of the glasses containing the minimum amount of the glass former P_2O_5 during production. The separation of the calcium-phosphate crystalline phases depletes the residual glass phases of calcium ions and enriches it with phosphate ions. Since the solubility of the crystallized glasses is determined, first and foremost, by the hydrolytically least stable glass phase, such a change of the chemical composition of the glass phase gives rise to a general increase of the solubility of the material.

Comparing the solubility indicators of glasses without Al_2O_3 (series I) and with Al_2O_3 (series II) shows a decrease of the solubility of aluminum-containing glasses. A similar result is observed in aluminum-containing calcium-borophosphate glasses [11]. In all probability, this is explained by the formation of a hydrolytically strong, mixed, aluminum-phosphorus-oxygen framework of the glass with fewer easily hydrolyzed P – O bonds. It is interesting that the introduction of Al_2O_3 makes it possible to regulate the solubility indicators, especially the migration of ions into solution, in the metaphosphate composition range (CaO : P_2O_5 about 1),

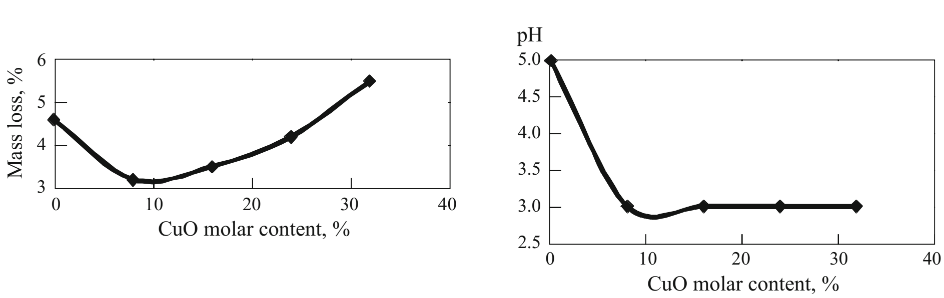

Fig. 4. Mass loss and pH of the solutions obtained after boiling of series III glasses.

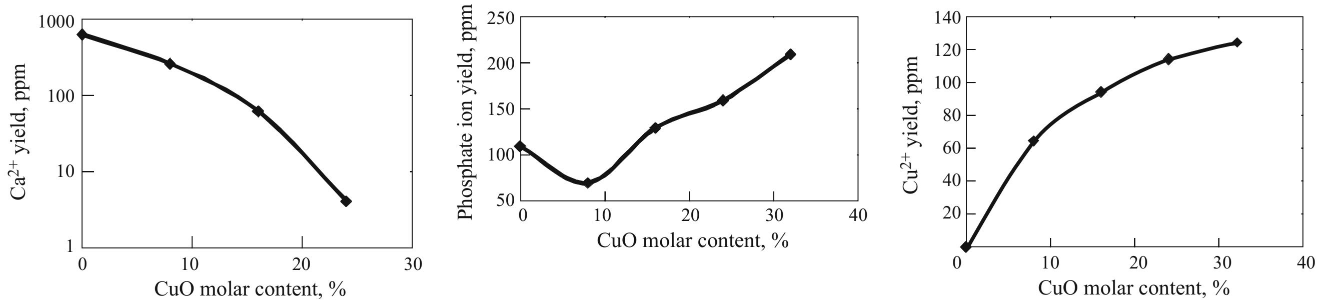

Fig. 5. Migration of calcium, phosphate, and copper ions in solution after boiling of series III glasses.

where changing the concentration of the basic components does not noticeably change the solubility of the glass (see Fig. 2).

The effect of the modifying cation replacement $Ca^{2+} \to Cu^{2+}$ on the solubility is reflected in the series II glasses (Figs. 4 and 5). The extreme compositions of this series contain one modifier cation — Ca^{2+} or Cu^{2+}. A comparative analysis of the solubility of these compositions with respect to mass loss and migration of the phosphate ions into solution shows that the substitution $Ca^{2+} \to Cu^{2+}$ increases the solubility of the glass, but this effect is much weaker than the effect of the ratio $CaO : P_2O_5$ (series I and II glasses). This is because Ca^{2+} and Cu^{2+} play the same structural role — such a substitution does not lead to a substantial restructuring of the phosphorus-oxygen framework of the glass. Nonetheless, a stronger interaction with the phosphate matrix than for copper ion is characteristic for the calcium ion because of its stronger force field Z/r^2 (Z and r are the charge and radius of the ion): for Ca^{2+} (CN = 6) $Z/r^2 = 2/0.104^2 \approx 185$ and for Cu^{2+} (CN = 8) $Z/r^2 = 2/0.087^2 \approx 264$. As a result, the hydrolytic stability of the calcium-phosphate glass is higher than that of the copper-containing glass. We note that the substitution $Na^+ \to Cu^{2+}$ in phosphate glasses results in lower solubility of the copper-containing glasses than in sodium-containing glasses [4], which confirms that the structural factors play the lead role in the analysis of the solubility of phosphate glasses.

For a partial substitution $Ca^{2+} \to Cu^{2+}$ the concentration dependence of the solubility, according to the mass loss and the yield of phosphate ions, is of an extremal character with a minimum at 8 – 10% CuO. This could be due to two cations, similar to the well-known polyalkali effect in glass. This extremum is not manifested in the concentration dependences of the yield of calcium and copper ions because of the variable content of these ions in series III glasses, i.e., in this case these dependences are not representative with respect to the solubility of the glass.

In summary, soluble calcium-phosphate glasses containing a biocidal component — copper oxide — were synthesized. It was established that phosphate glasses admit the introduction of more than 30% CuO, but to prevent crystallization the total amount of the modifier oxide (CaO + CuO) must not exceed 60%. The recorded migration of copper ions into water under the conditions of boiling (1 h) ranges from 60 to 125 ppm, which makes the glasses obtained biocidal.

It was found that the degree of solubility of the glasses can be controlled by varying their chemical composition. The ratio of the modifier cations and the glass former, determining the structure of the phosphorus-containing framework of the glass, has the largest effect on the solubility. The introduction of Al_2O_3 and substitution of copper oxide for calcium oxide have a much weaker affect on the solubility.

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